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Quarterly Technical Progress Report

No. 6329-18

on the

DEVELOPMENT OF METALLIZATION PROCESS

FSA Project, Cell and Module Formation Research Area

For the Period Ending

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ABSTRACT/SUMMARY

The initial evaluation of the matrix of pastes has been completed. Cells made with these pastes showed high contact and bulk resistance. Shunt resistance was not a problem.

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Section 1.0
INTRODUCTION

The objective of this contract is the optimization, evaluation, and demonstration of a novel metallization applied by a screen printing process. The process will be evaluated on both CZ and non-CZ silicon wafers.

Section 2.0
TECHNICAL DISCUSSION

Pastes have been received from Electrinx Inc. for evaluation. The matrix of pastes includes three frit types: No. 90, No. 494, and No. 450. Table 1 shows the composition of the three frits. Frit No. 450 is a typical lead borosilicate frit similar to those used in silver pastes. The other two frits have no lead, one contains barium and strontium (#494), and one does not (#90). Two different vehicles are used in the pastes, a conventional cellulosic vehicle V-38 and an acrylic vehicle V-26. Table 2 shows the composition of the vehicles. Some formulations are also prepared with and without Teflon powder, and one without frit. The following table summarizes the pastes:

<u>Paste</u>	<u>Frit 450</u>	<u>Frit 90</u>	<u>Frit 494</u>	<u>Teflon</u>	<u>V-26</u>	<u>V-38</u>
A			X		X	
B			X	X	X	
C		X			X	
D		X		X	X	
E			X			X
F		X		X		X
G		X				X
H		X		X		X
I	X				X	
J	X					X
K					X	
L						X

Table 1
FRITS INVESTIGATED

	<u>#450</u>	<u>#90</u>	<u>#494</u>
K ₂ O	1.80	0.41	2.20
Na ₂ O	2.36	6.33	2.03
CaO	5.98	13.97	9.35
MgO	0.32	0.76	0.41
PbO	31.72	-	-
Al ₂ O ₃	3.50	9.75	5.09
B ₂ O ₃	13.76	13.92	7.99
SiO ₂	40.56	54.86	55.66
SrO	-	-	6.08
BaO	-	-	11.19
MP ^O C	827	843	771

Table 2
VEHICLE FORMULATION

	<u>V-38</u>	<u>V-26</u>
α -Terpineol	43.62	88.00
Butyl Carbitol Acetate	43.62	
Ethyl Cellulose N-14	9.76	
Thixatrol ST	3.00	
Elvacite 2042		9.00
Troykyd XYZ		3.00

For the initial evaluation of the pastes cells were made with and without prefiring the paste at 600°C. Cells that were not prefired were dried at 250°C. The cells were then fired at 600°C for 5 or 10 minutes in H₂.

Pastes E, I, J, and L gave the best results. Figures 1-5 show typical curves from these cells. All other pastes produced cells with no curve shape and short circuit currents less than 300 milliamps. Figure 1 shows the E paste prefired and then fired for 5 minutes at 600°C. The prefire was generally better than drying as is seen in Figure 2 where the cell was dried. Cells produced from pastes I and J are considerably worse with high series resistance as can be seen in Figures 3 and 4. Paste J had a Pb-borosilicate frit and should have produced results similar to the Thick Film Systems' paste A. This discrepancy may be due to differences in the frit or changes in the sintering oven at Spectrolab. Paste L (Figure 5), which contains no frit, was comparable to E. In general the pastes with the cellulosic vehicle were superior. Pastes containing Teflon powder (B, D, F, and H) produced cells with no electrical output.

Contact and series resistance measurements were made on several of the cells produced. The pastes were also printed on ceramic substrates to determine bulk resistivity more accurately. Contact resistance was measured by dicing the cell into nine equal sections. This cutting creates sections which have six equivalent unconnected sections of metallization. By measuring the voltage drop at constant current (10 mA) between the outermost section and the other sections, a graph can be created as shown in Figure 6. The following equation applies to the graph:

Figure 1

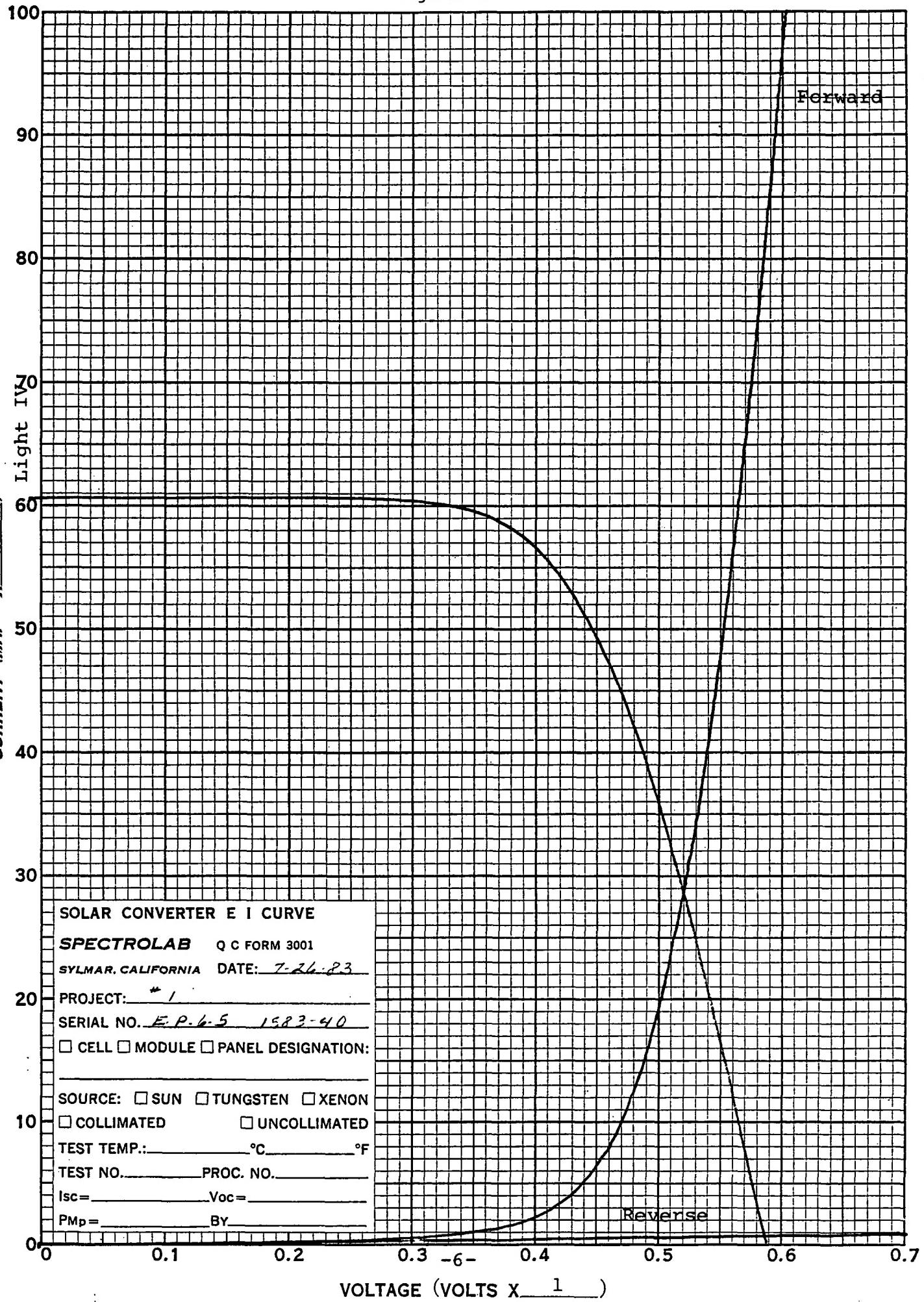


Figure 2

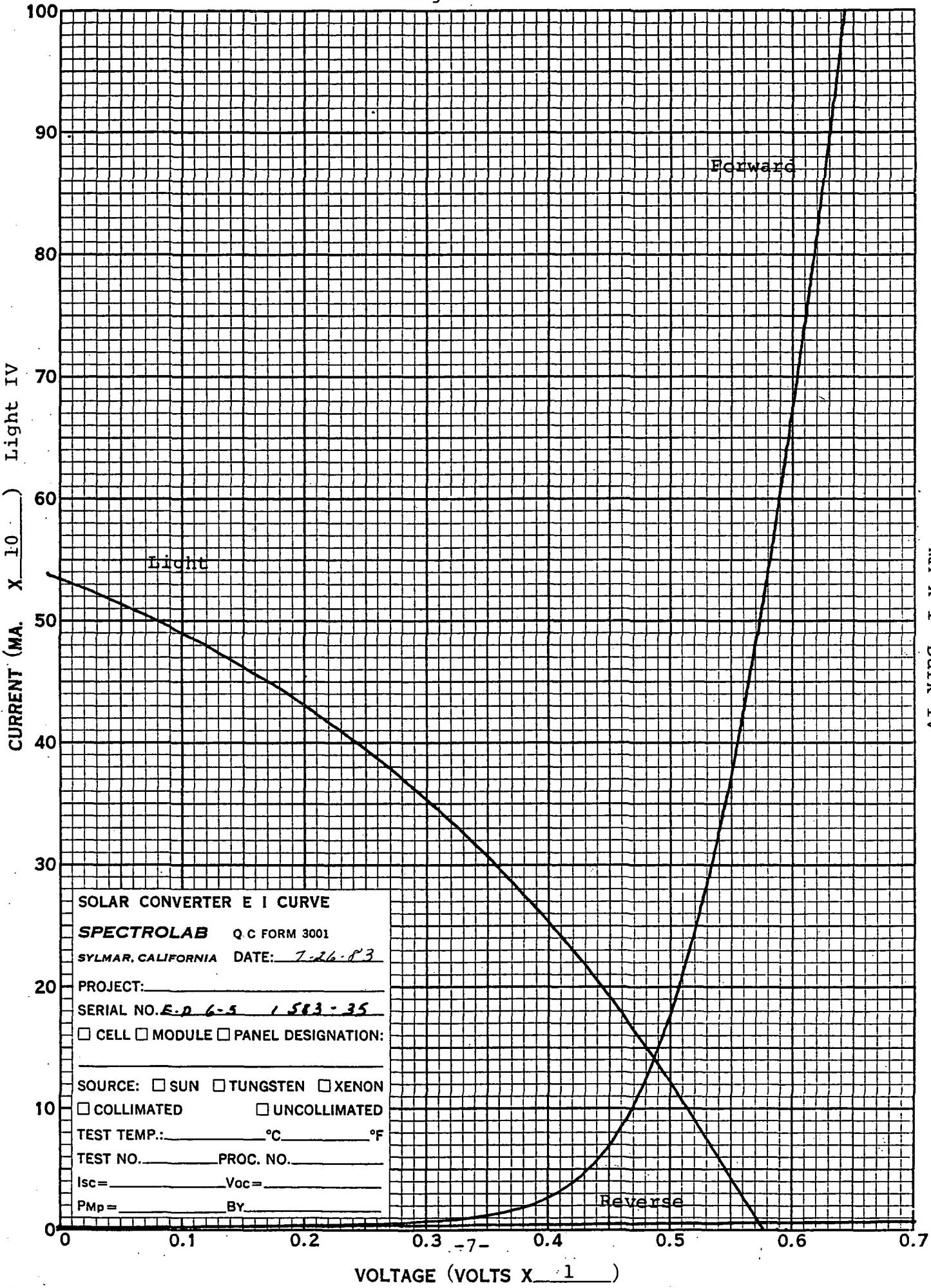


Figure 3

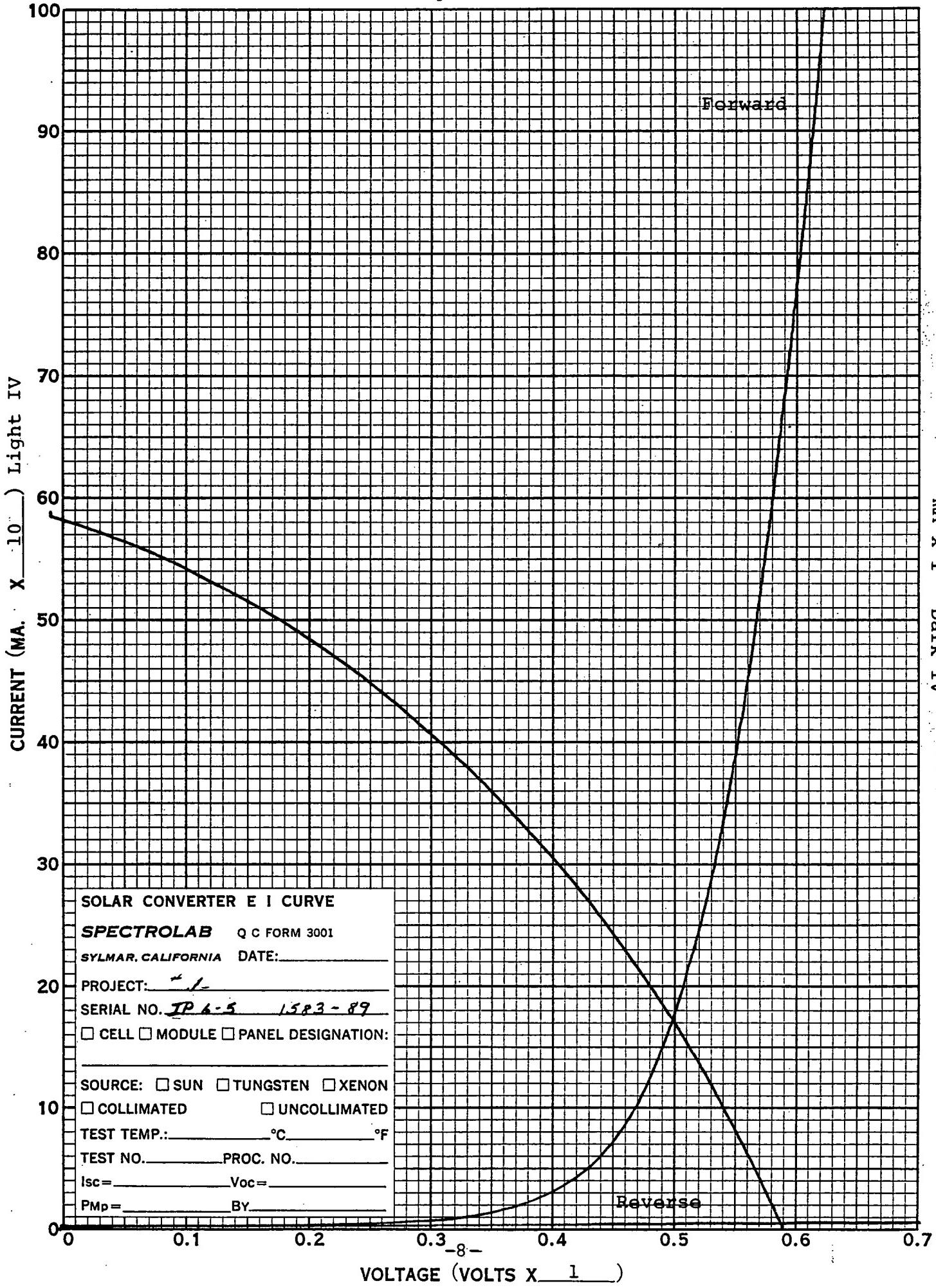


Figure 4

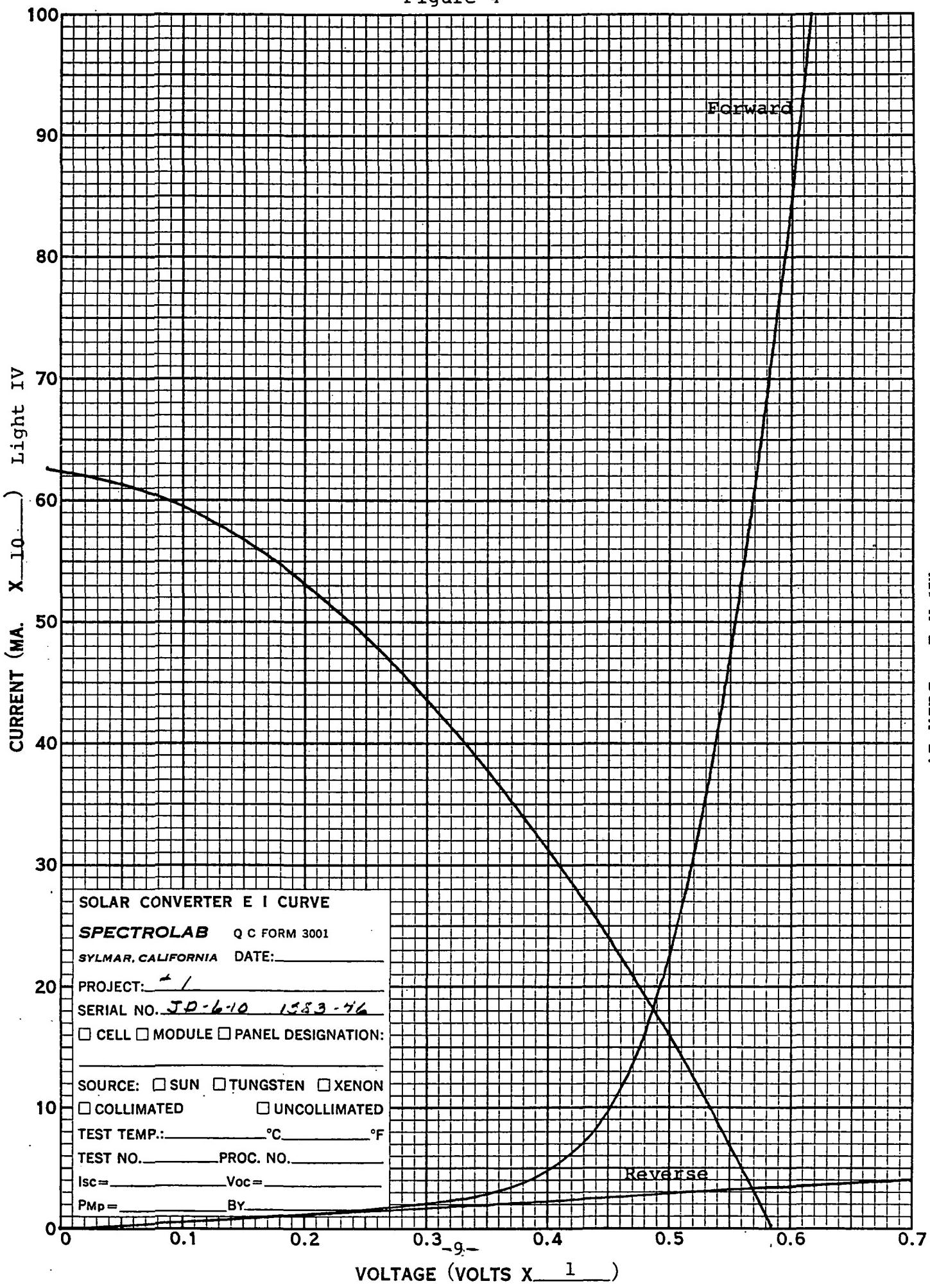


Figure 5

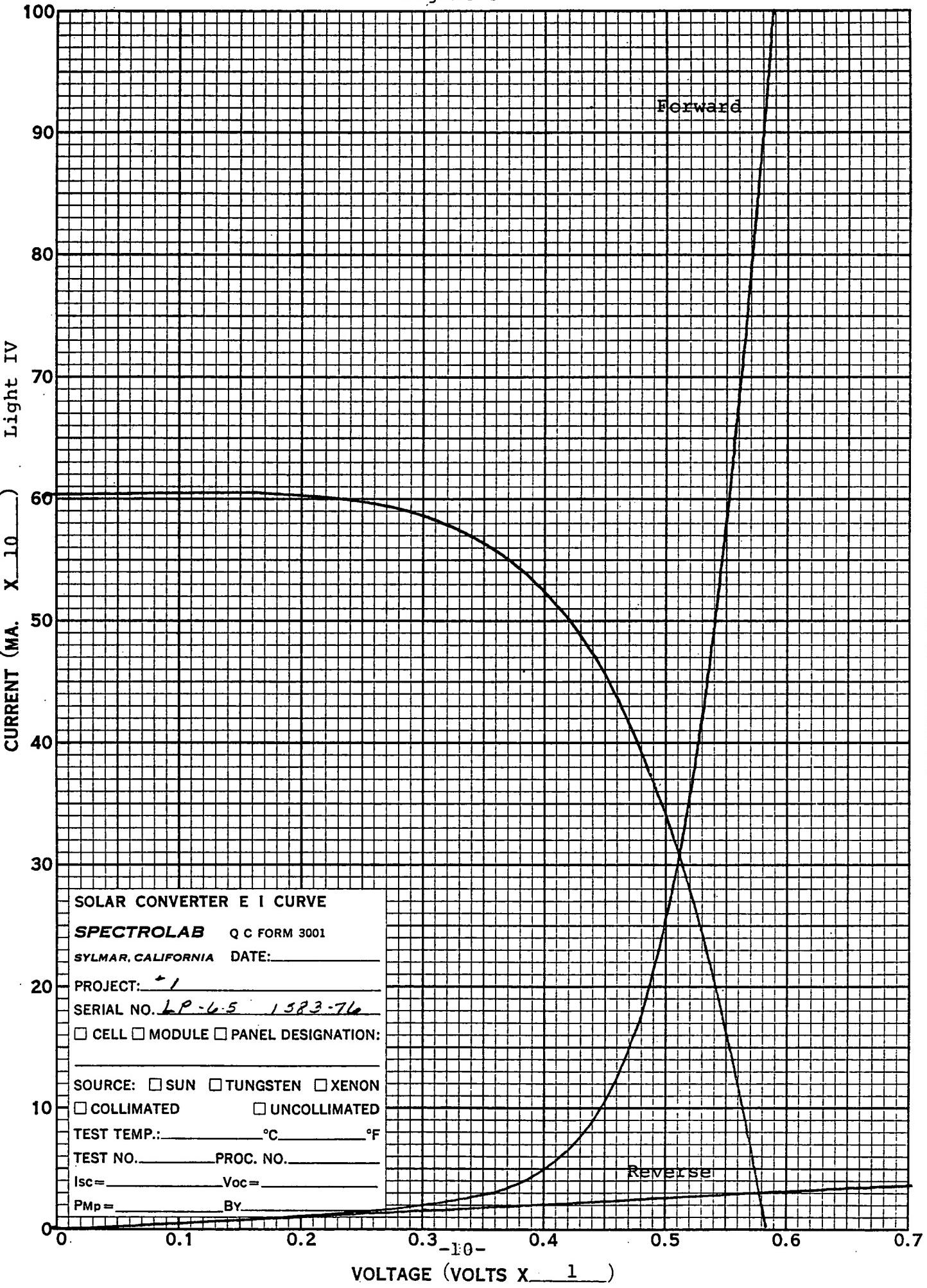
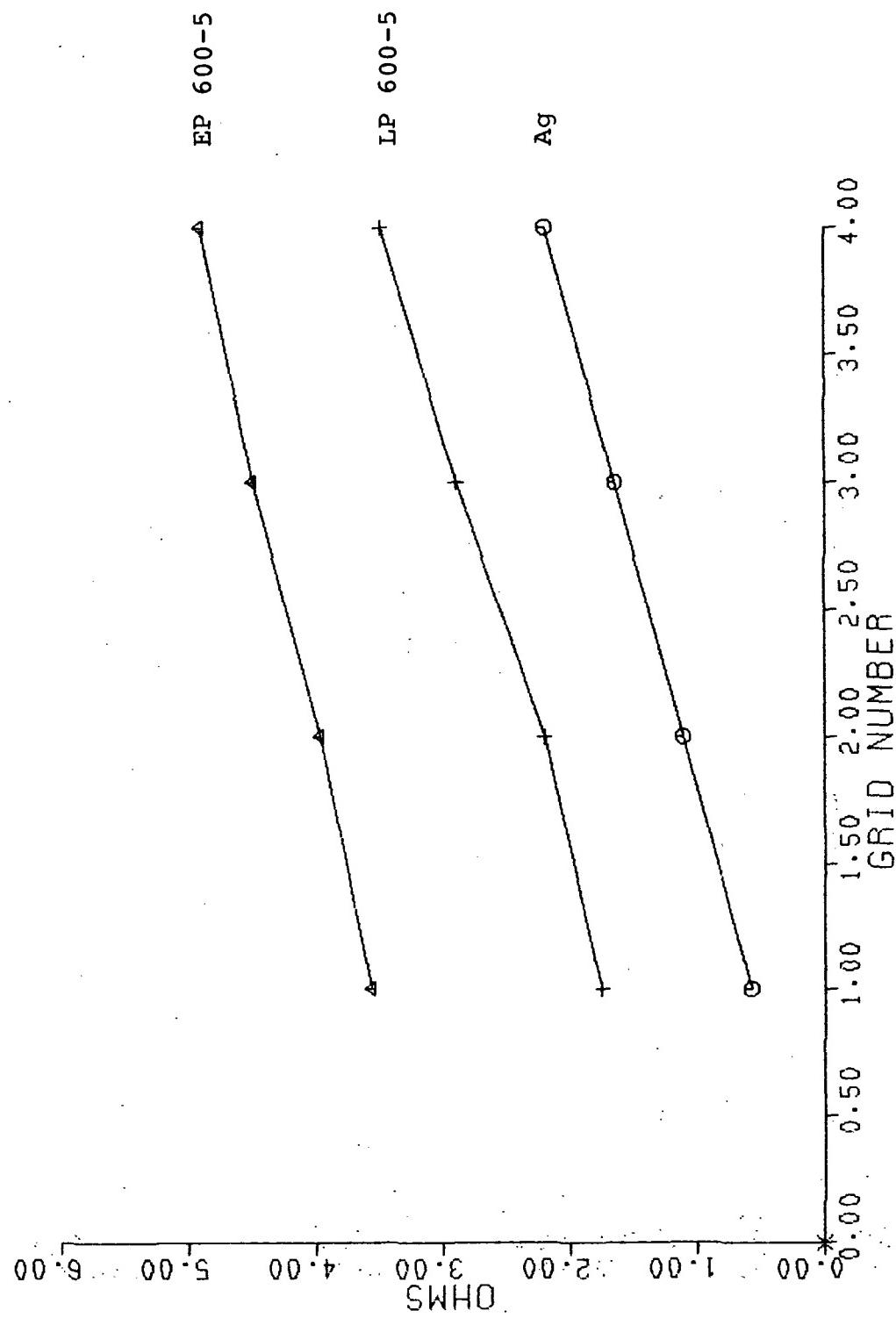


Figure 6
CONTACT RESISTANCE



$$V/I = nR_s + 2R_c$$

where

V = the measured voltage drop

I = the current (10 mA)

n = the grid number

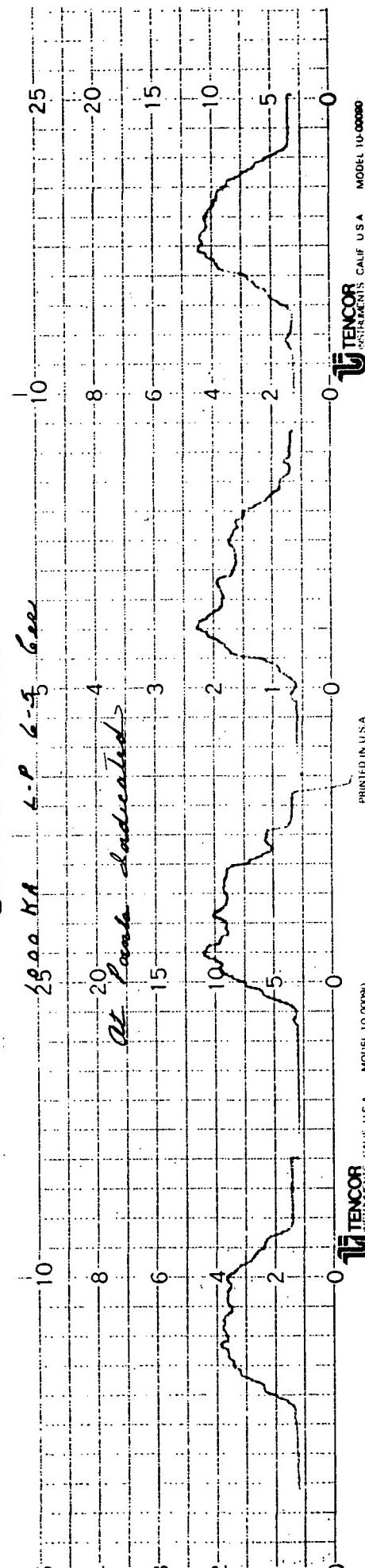
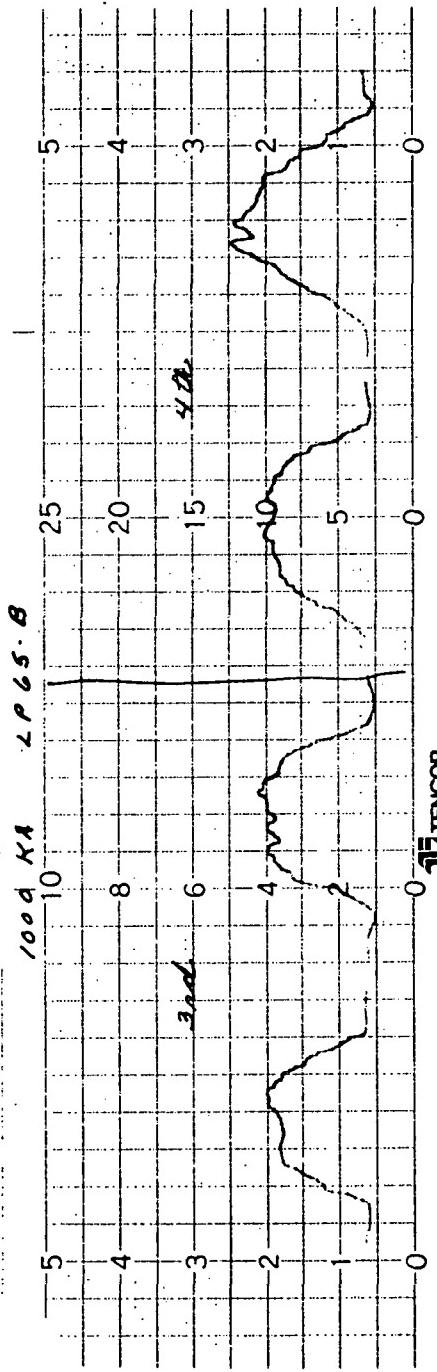
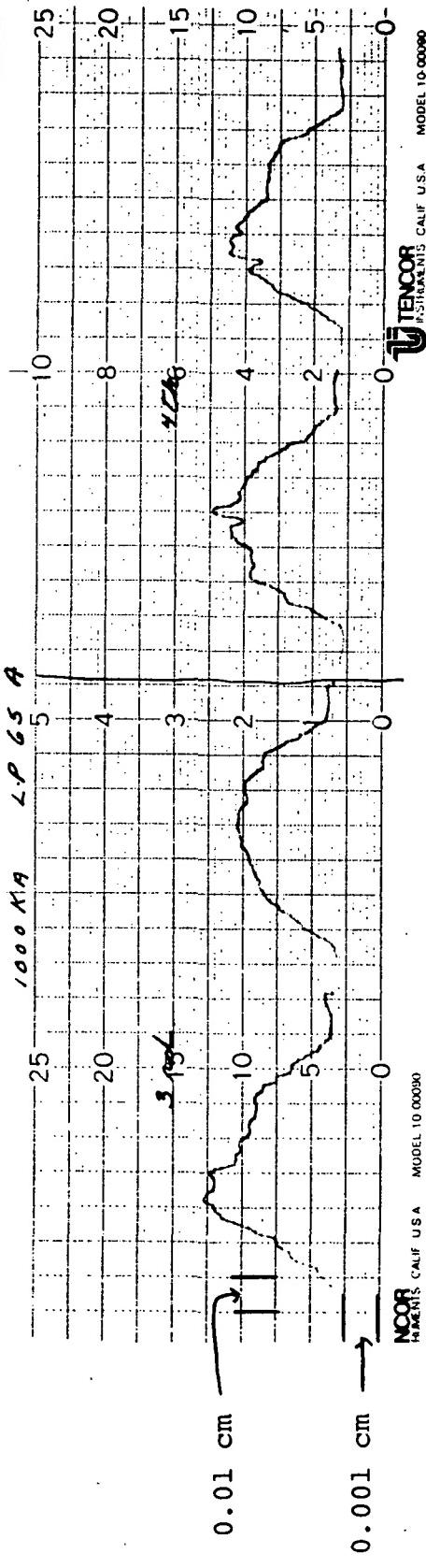
R_s = a bulk resistance between grids

R_c = the contact resistance for the grid
contact area

The y intercept of this line is twice the contact resistance over the contact area of a single section. The contact area on these samples was $0.68"$ \times the grid width measured by profilometry. This R_c value is not exact when the bulk resistivity of the metallization approaches that of the underlying silicon. That condition may occur in poorly sintered samples. Therefore the quantities determined must be used for relative, not absolute, measurements.

Bulk resistivity was determined using a four-point probe measuring voltage drop along a grid line. Measurements were also made on samples made using ceramic wafers in place of silicon. These samples did not turn out well due to the different thermal characteristics of the ceramic material. The time was not taken to optimize the ceramic firings. The cross section area of the grid lines was then measured using a profilometer. Figure 7 shows typical data from this device. The accurate determination of cross sectional areas of the grid lines is difficult if not impossible due to the irregularity in grid profiles. Thus resistance values determined must be viewed with caution. Using the cross-section area and the calculated resistance the bulk

Figure 7
PROFILOMETER DATA



resistivity can be determined. This number is accurate when the resistivity of the metallization is much less than that of the layer beneath it. The actual resistivity will be larger than the measured value when the resistivity of the metal approaches that of the substrate. Table 3 shows the results of bulk and contact resistivity measurements. The values that are measured on silicon should only be used for relative, not absolute, comparisons.

Table 3

Paste	Substrate	Prefire	Fire °C/Min.	Contact Resistance ohm-cm ²	Bulk Resistivity	
					Standard	~10 microhm-cm
Ag	Silicon	-	Standard	0.003	~20	
Ag	Ceramic	-	Standard	-		
E	Silicon	yes	600/5	0.15	~300	
E	Ceramic	yes	600/5	-	4000+	
E	Silicon	yes	600/10	0.14	~200	
E	Ceramic	yes	600/10	-	~1000	
E	Silicon	dry	600/10	0.21	~100	
E	Ceramic	dry	600/10	-	~1000	
I	Silicon	yes	600/5	0.20	~400	
I	Ceramic	yes	600/5	-	Friable	
J	Silicon	dry	600/10	0.20	~150	
J	Ceramic	dry	600/10	-	~300	
L	Silicon	Yes	600/5	0.05	~200	
L	Ceramic	Yes	600/5	-	~200	

Section 3.0

CONCLUSIONS AND RECOMMENDATIONS

There are no conclusions or recommendations to report for the period.

Section 4.0
ACTIVITIES PROJECTION

During the next quarter pastes will be evaluated that contain borane-pyridine and silver octoate. Paste formulations using MoO_3 in place of Mo metal will also be re-examined.